Hydrosilylation of Aldehydes and Ketones Catalyzed by Half-Sandwich Manganese(I) N-Heterocyclic Carbene Complexes

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Abstract: Easily available manganese(I) N-heterocyclic carbene (NHC) complexes, Cp(CO)$_2$Mn-(NHC), obtained in one step from industrially produced cymantrene, were evaluated as pre-catalysts in the hydrosilylation of carbonyl compounds under UV irradiation. Complexes with NHC ligands incorporating at least one mesityl group led to the most active and selective catalytic systems. A variety of aldehydes (13 examples) and ketones (11 examples) were efficiently reduced under mild conditions [Cp(CO)$_2$Mn(IMes) (1 mol%), Ph$_2$SiH$_2$ (1.5 equiv.), hv (350 nm), toluene, 25 °C, 1–24 h] with good functional group tolerance.

Keywords: aldehydes; hydrosilylation; ketones; manganese; N-heterocyclic carbene (NHCs)

A revolutionary challenge of the 21st century in homogeneous catalysis is the replacement of noble transition metals by their inexpensive, abundant and less toxic first row congeners. While the current development of iron-based catalysts offers an illustrative example,[1] the potential utility of manganese in the design of catalysts has received much less attention.[2] Notable exceptions include manganese coordination compounds acting as remarkable oxygen and nitrogen atom transfer reagents,[3] and a few cases where σ-alkyl(aryl)manganese compounds are engaged in C–C cross-coupling reactions.[4] Nevertheless, only a small number of the well known carbonyl-containing Mn(I)

complexes have found some applications in homogeneous catalysis,[5–11] including the reduction of carbonyl compounds.[12] We have recently shown that cationic[13] and zwitterionic[14] half-sandwich dicarbonyl iron(II) complexes [CpFe(CO)$_2$(NHC)] bearing an N-heterocyclic carbene (NHC) ligand and their nickel(II) analogues [CpNi(NHC)Cl][15] are active in the hydrosilylation of a variety of carbonyl substrates and imines. We report herein that neutral Mn(I) NHC complexes, isostructural with the previously described Fe(II) complexes, do catalyze efficiently the hydrosilylation of aldehydes and ketones under ambient conditions.

Cymantrene, CpMn(CO)$_3$, and its methylated analogue are inexpensive, industrially produced manganese organometallic compounds used as anti-knocking additives for gasoline.[16] Manganese(I) complexes Cp(CO)$_2$Mn(NHC) **1–6** (Scheme 1) were prepared in good yield (46–80%) upon photoinduced CO ligand substitution in CpMn(CO)$_3$ with the appropriate free NHC (UV light > 250 nm, 20 °C, 1–2 h) generated *in*

Complex	R	R'	yield [%]
1	Me	Me	56
2	*i*-Pr	*i*-Pr	52
3	Cy	Cy	46
4	Mes	Me	80
5	Mes	Mes	80
6	Dipp	Dipp	74

Mes: 2,4,6-trimethylphenyl; Dipp: 2,6-diisopropylphenyl

Scheme 1. Manganese(I) NHC complexes **1–6** used as pre-catalysts.

Table 1. Optimization of the parameters for the hydrosilylation of acetophenone catalyzed by half-sandwich Mn(I) complexes.[a]

Entry	Catalyst	Silane (equiv.)	t [h]	Conv. [%][b]
1	**1**	Ph_2SiH_2 (1.5)	2	60
2	**2**	Ph_2SiH_2 (1.5)	2	47
3	**3**	Ph_2SiH_2 (1.5)	2	10
4	**4**	Ph_2SiH_2 (1.5)	2	>97
5	**5**	Ph_2SiH_2 (1.5)	2	>97
6	**6**	Ph_2SiH_2 (1.5)	2	25
7[c]	**4**	Ph_2SiH_2 (1.5)	2	0
8[d]	**4**	Ph_2SiH_2 (1.5)	17	0
9	$CpMn(CO)_3$	Ph_2SiH_2 (1.5)	2	4
10	$Cp(CO)_2Mn(PPh_3)$	Ph_2SiH_2 (1.5)	2	20
11	$Cp(CO)_2Mn(PCy_3)$	Ph_2SiH_2 (1.5)	2	0
12		Ph_2SiH_2 (1.5)	2	2
13[e]	**4**	Ph_2SiH_2 (1.5)	17	86
14[e]	**5**	Ph_2SiH_2 (1.5)	17	89
15	**5**	Ph_2SiH_2 (1)	2	>97

[a] Catalyst (1 mol%), toluene (2 mL), ketone (0.5 mmol) and Ph_2SiH_2 (0.75 mmol) were added in this order and the solution was irradiated with UV (350 nm) for the indicated period of time.

[b] Conversion determined by GC after basic hydrolysis (MeOH, 2 M NaOH).

[c] Reaction performed at 100 °C without UV irradiation.

[d] Reaction performed under visible light irradiation (24 W fluocompact light bulb).

[e] 0.5 mol% of catalyst was used. 1-phenylethanol was detected in low yields by GC/MS and mixed with other unidentified compounds.

situ from the corresponding imidazolium salts and *t*-BuOK.[17]

The hydrosilylation of acetophenone was selected as a benchmark reaction for an initial screening of Mn(I) pre-catalysts (Table 1) in the presence of Ph_2SiH_2 as the reducing agent. To our delight, after only 2 h at room temperature under UV irradiation (350 nm), moderate to excellent ketone conversions were achieved for most of the NHC complexes **1–6** at 1 mol% catalyst loading. The complexes **1–3**, bearing *N*-alkyl substituents on the nitrogen atom, led to moderate conversions (entries 1–3, 10–60%).

More interestingly, complexes **4** and **5**, which incorporate an NHC ligand bearing at least one *N*-mesityl moiety, exhibit significantly higher catalytic activities (entries 4 and 5) as a full conversion was reached after 2 h. However complex **6**, bearing the bulkiest NHC ligand was found to be the least active system

(entry 6). UV irradiation was found to be crucial to activate the Mn(I) catalysts, which, otherwise, were neither active under thermal conditions (100 °C for 2 h) nor under visible light irradiation (entries 7 and 8). Very importantly, the presence of the NHC ligand in the manganese coordination sphere is essential to reach a significant catalytic activity, since cymantrene (entry 9) and dicarbonyl phosphine-type (entries 10 and 11)[18] or Fischer-type aminocarbene (entry 12) derivatives show only low activities. Decreasing the catalyst loading has a deleterious effect on the selectivity (entries 13 and 14). Finally, the quantity of silane could be decreased to 1 equiv. without any alteration of the conversion for the reduction of acetophenone (entry 15).

Besides, the screening of different silanes revealed that the initially chosen diphenylsilane is the reagent of choice for this reaction, though secondary and primary arylsilanes could also be used (for example, with $PhMeSiH_2$ and $PhSiH_3$, 94 and 81% conversions were obtained, respectively). Tertiary and alkyl-substituted hydrosilanes except Et_2SiH_2 are not suitable for this process (see the Supporting Information for a complete list of silanes tested). Noticeably the reaction also proceeds smoothly for aldehydes. Indeed, the reduction of benzaldehyde can be achieved within only 30 min in toluene, in the presence of Ph_2SiH_2 (1 equiv.) and the complex **5** (1 mol%) under UV irradiation (350 nm).

The optimized reaction conditions thus being determined, the potential of complex **5**, $Cp(CO)_2Mn$-(IMes), was evaluated in the hydrosilylation of a representative panel of aldehydes (Table 2) and ketones (Table 3), and the results were compared with those obtained with the isostructural Fe(II) complex $[Cp(CO)_2Fe(IMes)]I$.[13a,c]

The hydrosilylation of aldehydes (Table 2) was typically performed within 1 h (8 h for less reactive substrates), in toluene, in the presence of 1 mol% of **5** and 1.5 equiv. of Ph_2SiH_2. The reduction of benzaldehyde and its derivatives substituted in the *para*-position by either an electron-donating group such as NMe_2 or an electron-withdrawing group such as CN, proceeds quickly (1 h) and the corresponding alcohols were obtained in very good yields (entries 1–3). However, the reduction of the *meta*-fluorobenzaldehyde requires a longer reaction time (8 h). Interestingly, the reduction of the aldehyde functional group could be achieved in the presence of other carbonyl functions (namely ketone and ester) using only 1.05 equiv. of silane, albeit only in moderate yields due to the presence of over-reduced products (entries 4 and 5). Importantly, the aldehydes derived from heterocycles were also hydrosilylated with excellent conversions (entries 7–9), surpassing the Fe(II) catalyst $[Cp(CO)_2Fe(IMes)]I$ in the case of 2-formylpyridine (>97% conversion in 1 h, entry 9, *vs.* 88% after

Table 2. Scope of aldehyde hydrosilylation catalyzed by manganese(I) NHC complex **5**.[a]

1) **5** (1 mol%), Ph₂SiH₂ (1.5 equiv.)
toluene, 25 °C, 1 h, UV (350 nm)
2) hydrolysis: MeOH, 2 M NaOH

$$R' \overset{O}{\underset{H}{\bigvee}} \longrightarrow R' \overset{OH}{\bigvee}$$

Entry	Substrate		Conv. [%][b]	Yield [%][c]
1	(4-R-benzaldehyde)	R = H	> 97	90
2		R = NMe₂	> 97	90
3		R = CN	> 97	89
4		R = COCH₃	> 97[d,e,f]	55
5		R = COOCH₃	> 97[d,e]	51
6	(3-F-benzaldehyde)		15 / 92[d]	– / 90
7	(furfural)		42 / > 97[d]	– / 97[g]
8	(N-pyrrole-CHO)		10 / > 97[e]	– / 54
9	(pyridine-2-CHO)		> 97	97[g]
10	Ph-CH=CH-CHO		> 97[d,e]	80
11	(alkenyl-CHO)		> 97[d,e]	71
12	(citronellal)		> 97[d,h]	70
13	Ph-C≡C-C₆H₄-CHO		> 97	88

[a] Pre-catalyst **5** (1 mol%), toluene (2 mL), aldehyde (1 mmol) and Ph₂SiH₂ (1.5 mmol) were added in this order and the solution was irradiated with UV light (350 nm) for 1 h.
[b] Conversion determined by ¹H NMR after basic hydrolysis.
[c] Isolated yield.
[d] Reaction was carried out for 8 h.
[e] 1.05 equiv. Ph₂SiH₂.
[f] 40% of the corresponding diol was detected in the crude mixture by ¹H NMR.
[g] Yield determined by ¹H NMR on the silylated alcohol using DMF as an internal standard.
[h] 2.5 equiv. Ph₂SiH₂.

Table 3. Scope of ketone hydrosilylation catalyzed by manganese(I) NHC complex **5**.[a]

1) **5** (1 mol%), Ph₂SiH₂ (1.5 equiv.)
toluene, 25 °C, 4 h, UV (350 nm)
2) hydrolysis: MeOH, 2 M NaOH

$$R' \overset{O}{\underset{}{\bigvee}} \longrightarrow R' \overset{OH}{\bigvee}$$

Entry	Substrate		Conv. [%][b]	Yield [%][c]
1	(4-R-acetophenone)	R = H	> 97	65
2		R = OMe	> 97	97
3		R = Me	> 97	92
4		R = F	> 97	83
5		R = Cl	0	–
6		R = Br	0	–
7	(2-methylacetophenone)		18 / > 97[d]	– / 95
8	(2-acetylnaphthalene)		> 97	96
9	(acetylferrocene)		0 / > 97[d]	– / 75
10	(4-phenyl-2-butanone)		96	80
11	(dialkyl ketone)		59 / > 97[d]	– / 93
12	(1-tetralone)		54 / > 97[d]	– / 57
13	(benzalacetone)		0 / > 97[d]	– / 47[e]

[a] Pre-catalyst **5** (1 mol%), toluene (2 mL), ketone (1 mmol) and Ph₂SiH₂ (1.5 mmol) were added in this order and the solution was irradiated with UV light (350 nm) for 4 h.
[b] Conversion determined by ¹H NMR after basic hydrolysis.
[c] Isolated yield.
[d] Reaction was carried out for 24 h.
[e] 22% of the corresponding 4-phenyl-butan-2-ol was also isolated.

15.5 h at 70 °C at the same catalyst loading).[13a] Finally, this catalytic system was also shown to be tolerant to conjugated or terminal alkenyl and alkynyl moieties as neither isomerization nor reduction of the C=C bond was detected by ¹H NMR in the crude mixture (entries 10–13).

The scope of the reduction of ketones was then investigated (Table 3). Both aromatic (entries 1–4, 8) and aliphatic (entry 10) ketones were reduced in good

to excellent yields at room temperature, typically within 4 h. For less reactive substrates, such as *ortho*-methylacetophenone, acetylferrocene, dialkyl or cyclic ketones (entries 7, 9, 11, 12, respectively), an extension of the reaction time up to 24 h proved to be nec-

essary to achieve a complete conversion. The unexpected bias of the catalytic system regarding chloro- and bromo-substituents (entries 5 and 6) may be attributed to a rapid photochemical decomposition of **5** in the presence of these substrates.[19] It must be noticed that in the case of the conjugated 4-phenylbut-3-en-1-one (Table 3, entry 13), 22% of the fully reduced alcohol was detected in the ^{1}H NMR of the crude mixture, in contrast with the conjugated aldehyde (Table 2, entry 10).

A comparative analysis of the results obtained with the present Mn(I) NHC complexes and those previously reported for the cationic Fe(II) NHC complex [Cp(CO)$_2$Fe(IMes)]I reveals the superiority of the new system in terms of catalyst loading (1 mol% *vs.* 2 mol%), temperature (25°C *vs.* 50–70°C) and reaction time (4 h *vs.* 16 h). For example, the hydrosilylation of *para*-methoxyacetophenone proceeds almost quantitatively with **5** (Table 3, entry 2), whereas 61% (in toluene)[13a] and 86% (neat conditions)[13c] conversions were achieved using the cationic Fe(II) complex.

At the present stage of our investigation, the mechanism of the hydrosilylation process catalyzed by Mn(I) NHC complexes has not yet been clarified, though the initial activation step is very likely a photochemical CO dissociation giving an unsaturated 16-electron intermediate.[17] A GC monitoring of the hydrosilylation of acetophenone (Figure 1) catalyzed by **5** revealed the occurrence of an induction period. Further studies are currently underway in order to get mechanistic clues reflecting this feature.

In conclusion, we have disclosed a new and efficient catalytic system for the hydrosilylation of aldehydes and ketones under ambient conditions based on readily available Mn(I)/NHC complexes deriving from cymantrene. This catalytic system is superior to the one using isostructural iron(II) analogues[13,14] and comparable with the one based on their nickel(I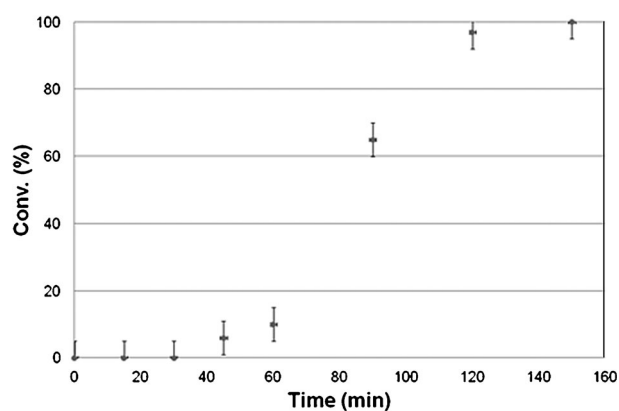I) analogues.[15] This family of catalysts appears very promising for the development of an enantioselective version of this transformation[20] based on well known chiral NHC ligands.[21]

Experimental Section

General Procedure for the Hydrosilylation of Ketones Catalyzed by Mn(I) NHC Complex 5

A 10-mL oven-dried Schlenk tube containing a stirring bar, was charged with Cp(CO)$_2$Mn(IMes) **5** (4.8 mg, 0.01 mmol). After purging with argon (argon–vacuum 3 cycles), toluene (2 mL) was added followed by Ph$_2$SiH$_2$ (279 μL, 1.5 mmol) and ketone (1 mmol). The reaction mixture was irradiated under UV (350 nm) for 1 h. At the end of the reaction MeOH (2 mL) and 2M NaOH (2 mL) were added consecutively under vigorous stirring. The reaction mixture was stirred for further 2 h at room temperature and was extracted with diethyl ether (3×10 mL). The combined organic layers were dried over anhydrous MgSO$_4$, filtered and concentrated under vacuum. The residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether mixture (10 to 50%) to afford the desired product with >95% purity.

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